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ABSTRACT

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The history and principles of the double monitoring type mass spectrometer developed by Mattauch and Herzog and others is reviewed. The device developed by the authors (JMS-01) has a resolution of 5000. The other specifications are given in Table 2. The electrical, vacuum and mechanical systems, as well as the various types of spark ionic sources are described. Section 3 gives a detailed description of micro-analysis by means of the spectrometer. The methods of preparing metallic, non-metallic, semiconductor and powder samples are described. Section 3.2 discusses photographic dry plates used in the spectrometer. Methods of obtaining good spectra for various ions are given in section 3.4. Section 3.4 discusses qualitative analysis using the spectrometer. Section 3.6 discusses quantitative methods. 3.7 treats the relative sensitivity ratio. Section 3.8 describes a measurement of an iron sample.

Author

1. Introduction

The conventional methods, which are widely used, to detect /1778* very small quantities of the composition elements in a solid specimen are radiation spectral analysis and radiochemical analysis. It is well known that both of these methods give an effective measure on the order of ppm or less. Needless to say, each of these methods is excellent and is surely an outstanding method of analysis. The former is one of the most popular methods, but sometimes fails in a good quantitative analysis. Generally, the possible detection limit differs greatly from element to element and ranges from 10 to 1 ppm when a D.C. arc or an A.C. arc is used. The possible detection limit is decreased when a spark is used for the quantitative analysis. To increase this limit, many methods have been worked out for specific elements. These are a method of concentrating the specimen chemically, a method of analyzing the absorption spectrum by the use of a specific light source, the hollow-cathode discharge method or the microwave discharge method. Generally speaking, we can only attain a detection limit on the order of 0.1 ppm, even though we use these methods. In the case of the radiochemical analysis, it is possible to detect the order of ppb by using a flux of magnitude of 10^{11} cm^{-2} sec^{-1} for specific elements such as Na, Al, Sc, V,

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* Note: Numbers in the margin indicate pagination in the original foreign text.

As, Pb, Br, Ga, I, La, Au, Sb, W, etc.

A stronger flux makes a finer analysis possible. The radiochemical analysis method has a high sensitivity to In, Sm, Eu, Dy, Ho, Lu, Re, Ir, etc. On the other hand, for S, Ca, Fe, Nb, Pb, etc., we can, at most, detect on the order of ppm. Thus, this method has the following defects: the sensitivity of detection differs for different elements. We need a special experimental apparatus, such as an atomic reactor to activate the specimen. Some elements require much time for activation, and their life is quite short. Actually, for some kinds of lighter elements, this method cannot be used for analysis. Furthermore, there are some cases in which it is difficult to isolate each element even by the use of a pulse height analyzer for a specimen containing many elements. The following method of analysis, using a spectrometer, is used to analyze the specimen both quantitatively and qualitatively: the solid specimen is ionized with a spark and the elements are detected separately by mass spectroscopy. This method requires only simple handling of the specimen and generally makes it possible to measure very small amounts on the order of less than ppm, independent of the types of the elements, with an expenditure of 1 mg of the sample. It has been shown by Hannay (Ref. 1), Shaw (Ref. 2), and Hipple (Ref. 3) that this kind of microanalysis can be carried out using a Mattauch-Herzog type mass spectroscope. Only recently have commercial mass spectrometers which meet the above-mentioned purpose been produced. At last the time is ripe for the use of such kinds of apparatus in

our country. This method has the convenience of radiation spectroscopy and the high sensitivity of radiochemical analysis, and is considered to be a good method of analyzing small amounts of component elements in a solid. This method has become of practical use only very recently, even though it has been known to be an excellent method. The reasons are as follows: high-vacuum pressure technology has been developed, and, consequently, the difficulties with the vacuum technique have been overcome. Recently, electronic technology has developed tremendously. Good electronics are necessary to obtain good performance. Research in pure metals, semiconductors, etc., which require microanalysis, has been rapidly broadened with advances in space technology and industry.

Today this type of apparatus, which chemical engineers can handle with ease, has been developed and used in England, the U.S.A., Japan, and Germany. There is an indication in our country that /1779 this type will become very popular in the near future. The authors completed the JMS-01 type double beam mass spectrometer as an example of this type of apparatus last year. Since then, we have performed microanalysis experiments. We will now describe in detail the principle of this type of apparatus and its application to analysis.

2. Mattauch-Herzog Type Double Monitoring Mass Spectrometer

2.1 Summary

This type of mass spectrometer was first developed by Mattauch and Herzog (Ref. 4, 5) in 1934.

Bambridge-Jordan and Nier subsequently invented different types of the double monitoring mass spectrometer. The Mattauch type is designed to monitor all ions twice. It is superior to the single monitoring device which performs only the directional monitoring by a uniform magnetic field, because it is capable of making the ions of different energy converge to one point, thus giving a sharp image, and can focus ions whose mass varies over a wide range on the same plane.

Mattauch himself showed two examples of devices of this type, one of which is shown in Figure 1 and is extensively used today.

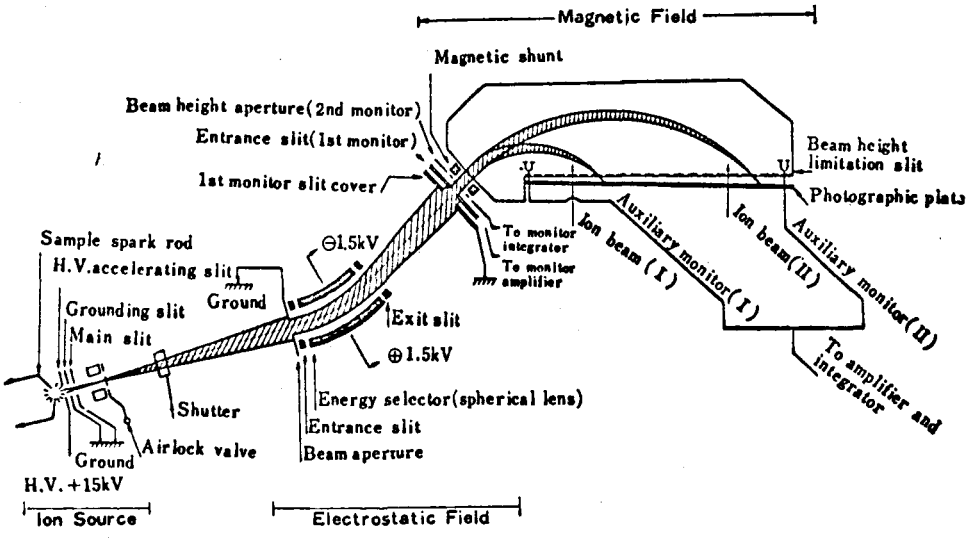

Figure 1

Principles of the Mattauch-Herzog Type Double Monitoring Mass Spectrometer for the Analysis of Extremely Small Quantity of Samples

For the purpose of analysis of solids, it is ideal to ionize every component in a uniform way. The ionizing method which is known to be close to this ideal one is the spark method, which ignites sparks among materials. However, the ions supplied by such an ion source acquire different initial speeds and their small mass difference can only be distinguished by a mass spectrometer with high monitoring capability such as the Mattauch-Herzog type. This capability of resolving small mass differences is measured as resolution. This resolution R is given by $R = M/\Delta M$ if the mass spectrometer can separate ions having ratios M/e from those having ratios $(M+\Delta M)/e$.

In the case of the analysis of solids, this resolution must be more than 2,000 (Table 2), since it becomes necessary to resolve the multiple spectrum lines of the ions from those of the spark ionic source.

Such high resolution can be expected only of the mass spectrometer of the double monitoring type, which has the capability of directional and speed focusing.

TABLE 1

EXAMPLES WHICH REQUIRE HIGH RESOLUTION

(1)	(2)
$^{1}H_{2}$-^{2}D	1300
^{14}N-$^{29}Si^{+2}$	960
^{24}Mg-$^{12}C_{2}$	1600
^{32}S-$^{16}O_{2}$	1800
$^{12}C^{16}O$-$^{14}N_{2}$	2500
^{27}Al-$^{54}Fe^{+2}$	2300
^{92}Mo-$^{70}Ge^{16}O$	12000

(1)-Double Line Ionic Structure; (2)-Required Resolution.

If the resolution is over 2,000, almost all elements can be analyzed. However, in special cases, the analytical capability must be reinforced. The spark ionic source for the analysis of solid substances has the advantage of uniform ionization. On the other hand, such an ionic source has the disadvantage of an unstable ion beam. Thus, the mass spectrometer for this purpose must be of the spectrographic type which is capable of simultaneously detecting various ions spread over a wide range. It is well-known that the Mattauch-Herzog type and Reuterswärd type fulfill all these requirements. The type in practical use is the Mattauch-Herzog type and its modifications. The device of this type possesses excellent properties, and many kinds are used in laboratories besides the original one designed by Mattauch (Ref. 4) himself. In most cases, they have a cylindrical electric field with a rotation angle of 31°50' and a magnetic field with a rotation angle of 90°, and their image plane is placed along the 135° line with respect to the plane of the incident magnetic field. The electric field is connected in series and has a direction opposite the rotation. Also, the exit point of the ions is placed at the focus of the electric field, and the incident angle with respect to the electromagnetic field is zero degrees.

2.2 Device In Use

As an example of the device of this type, the JMS-01 type double monitoring mass spectrometer designed by the authors will now be discussed. (Figures 1 and 2.) The specifications are shown in Table 2.

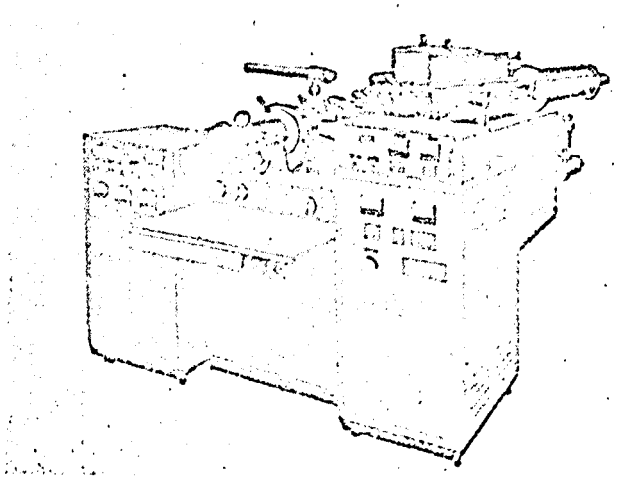

Figure 2

Diagram of the Device

In this device, some improvements were added to the original Mattauch system. As attempted by Herzog (Ref. 7) and Edwald (Ref. 8), a /1780 spherical lens is used for the electrode of the electric field. Since the beam along the z axis is monitored by the electric field, the sensitivity is improved. Also, dispersion of the beam towards the z axis is prevented, thus reducing the variation of sensitivity due to the length of the ionic trajectory. When this lens is used, the theoritical value of resolution becomes $M/\Delta M = a_c/S$ (a_c: revolving radius of ions in the electric field; S: slit width). The distance between the slit and the electric field is $\sqrt{3}\, a_c$. Theoretically, $M/\Delta M = 10{,}000$ for a slit width of 20μ.

Also, the variable slits α,β are used, which control the direction dispersion angle and speed dispersion angle, so that the device can be operated either at high sensitivity or high resolution. Besides, by switching, it can be used for anions. This feature is expected to

TABLE 2

SPECIFICATIONS OF JMS-01 TYPE DOUBLE MONITORING MASS SPECTROMETER

Resolution	5,000
Sensitivity	10^{-8} (atomic ratio)
Detectable Mass Range at One Time	1:36
Dry Plate	Ilford Q_2 380x50x1 (mm^3)
Number of Exposures	Number of Spectral Lines Acceptable in One Dry Plate is 15
Length of Spectral Line	2 mm
Extra Exhausting Box for Dry Plate	8 Plates Inserted
Printing Temperature	150° C at its Highest
Ionic Source	
Accelerating Voltage	15 kV, 7.5 kV, 3.75 kV; 3 Stages
Stability	1%/10 min
Frequency	About 1 Mc
Peak Voltage	About 100 kV
Instant Power	About 100 kW
Pulse Width	10μs, 20μs, 60μs, 80μs, 100μs; 6 Stages
Pulse Repeating Frequency	1 c/s, 3 c/s, 10 c/s, 30 c/s, 100 c/s, 300 c/s, 1 kc/s, 3 kc/s, 5 kc/s; 9 Stages
Electric Field:	
ϕ_e	30°
a_e	200 mm
Voltage Stability	40 ppm/10 min
Voltage	∓ 1.5 kV, ∓ 750 V, ∓ 375 V; 3 Stages
Magnetic Field:	
ϕ_m	90°
Intensity	Maximum 12,000 Gauss
Power	About 150 W
Current Stability	20 ppm/10 min
Maximum Revolving Radius	315 mm
Minimum Revolving Radius	52 mm
Gap of Magnetic Field	5 mm
Exhausting System:	
Oil Dispersing Pump With Trap	6" 2 Sets
Ion Pump	40 ℓ/s 1 Set
Rotary Pump	150 ℓ/min 1 Set
Rotary Pump	75 ℓ/min 1 Set
Trap for Liquid Nitrogen	Two Sets

TABLE 2 (Cont.)

Packing	Biton
Consumption of Liquid Hydrogen	About 16 ℓ/day
Attainable Degree of Vacuum at Ionic Source	1×10^{-6}
Attainable Degree of Vacuum at Electric Field	3×10^{-7}
Attainable Degree of Vacuum at Magnetic Field	7×10^{-7}

be important in research, because various useful effects of the mass spectroscopic analysis of anions have been discovered in recent years (Ref. 9).

2.2.1 Electric System

Inevitably, this kind of device has very complicated electric circuits. Especially the stability of each field must be maintained, such that $M/\Delta M \geqq {}^1/_2 \cdot H/\Delta H$ and $M/\Delta M \geqq E/\Delta E$, by a rigid control. Hence, the system must be designed in such a way that one can perform the measurement using electronic circuits without worrying about the stability of fields.

2.2.2 Vacuum System

The mass spectrometer is a device which requires a high degree of vacuum. For this purpose, a good design for the separation scheme and the preparatory exhausting system is necessary to maintain a high vacuum at the time when samples of the ionic source or dry plates are exchanged at the image plane. These problems are taken care of in our device, and the convenience of operation and maintenance is increased by the use of the ion pump (Figure 3).

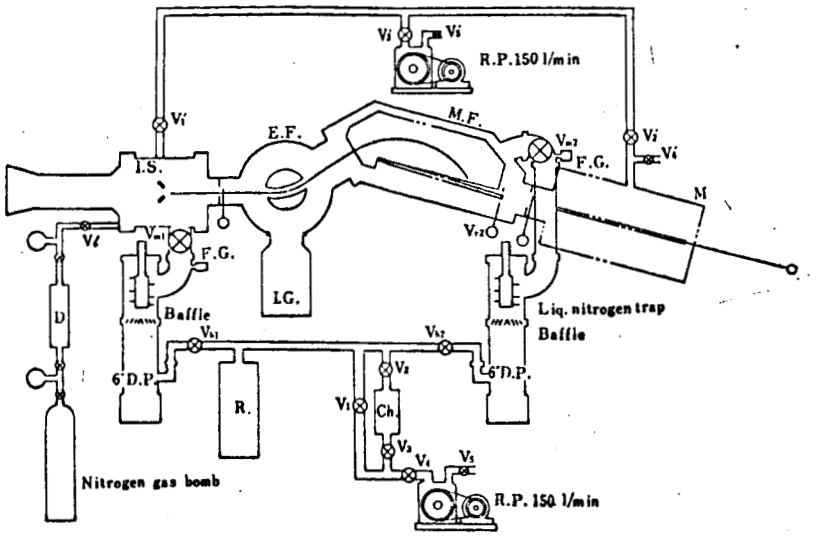

Figure 3

Exhausting System

R.- Reserver; V.- Vacuum Valve; F.G.- Gauge; M.- Extra Exhausting Box for Dry Plate; I.S.- Ion Source; E.F.- Electric Field; M.F.-Magnetic Field; I.G.- Ion Pump 40 ℓ/sec; D.P.- Oil-Dispersing Pump; R.R.- Oil Rotary Pump; D.- Desiccator; Ch.- Charcoal Trap

2.2.3 Mechanical System

The mechanical system is the core of the device. Whether the theoretical capability can be achieved or not depends entirely on the design of this system. Care must be exercised to maintain uniform electric and magnetic fields, precision of the structure, its stability, and a restoring force if heat distortion occurs.

The devices presently on the market are the ones produced by the Mitsubioki Electric Company of Japan, the 21-110 of the C.E.C. of the U. S. and the MS-7 of the A.E.I. of England. Also the German ATLAS-SM-1 is expected in the near future.

2.3 Spark-Type Ionic Source

As mentioned before, a spark ionic source is necessary to ionize samples uniformly. The following methods are commonly adopted for this purpose.

2.3.1 R.F. Spark

A short pulse of high frequency voltage around 1 Mc is applied between the sample electrodes placed in the ionic source, which evaporates and ionizes the sample instantaneously. This method was attempted by Dempster (Ref. 10) for the first time and is a widely used form of ionic source.

In practice, a pulse, as shown in Figure 4, is applied to the samples. Its actual wave form observed by synchro-scope is shown in Figure 5. /1781

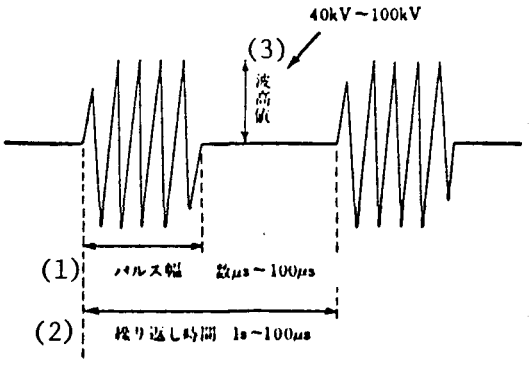

Figure 4

High Frequency Pulse Wave Form I of Spark From Ionic Source

(1)-Pulse Width: Several μs ～ 100μs; (2)-Repeating Time: 100μs ～ 10^6μs; (3)-Amplitude: 40 kV ～ 100 kV

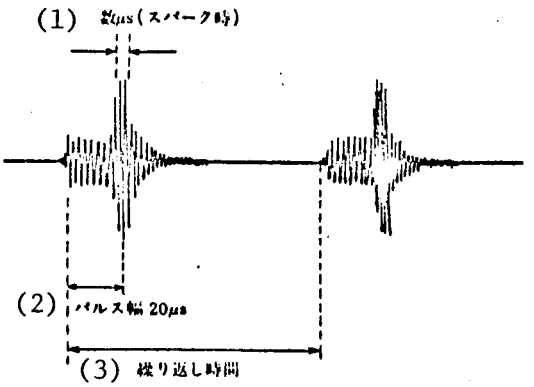

Figure 5

R.F. Pulse Wave From II of Spark From Ionic Source (Spark Time)
(1)-Spark Time: several μs; (2)-Pulse Width: 20μs; (3)-Repeating Period

Since this spark must be excited in a vacuum, an extremely high voltage is required. However, excessive power may cause overheating of the sample, and selective properties in the ionization of elements may come out depending upon the kind of samples. Therefore, a suitable choice of pulse-width and repetition frequency becomes necessary in such cases. As for metals in general, a pulse-width on the order of μ sec (the actual duration of spark is shorter than this) and a repetition frequency of 1 cps ~ 3 kc are best. The latter may vary depending upon the magnitude of the ionic beam. Semi-conductors may become heated up unless the repetition frequency is reduced.

2.3.2 D.C. Spark

There is a simple method of applying an electric impulse by means of a pulse transformer. However, this produces more ions of multiple valence. Hence, the R.F. Spark method is superior to this method for analysis purposes.

2.3.3 Vibration-Type Spark Ionic Source

This method utilizes an arc produced by first letting the sample electrodes make contact with each other, and then by switching them on and off by vibration. This was studied by Hintenberger, et al. (Ref. 11) and was reported to have a good repeating property. This method also stimulates the generation of multiple valence ions (especially of valence 2). An improvement for the purpose of reducing this effect was attempted by using an L.C. circuit.

At the time, the following properties of the R.F. Spark method of 2.3.1 is still under study: energy distribution of generated ions and its generation ratio of multiple valence ions. Rigorously speaking, it cannot be said that it produces a uniform ionization. However, under some constraints, repeating properties sufficient for semi-qualitative analysis have been achieved. Further improvement of qualitative properties can be expected as well as progress in ionic source research.

3. Practical Method of Micro-Analysis by the Mattauch-Herzog Type Double Monitoring Mass Spectrometer

3.1 Treatment of Samples

Since this type of device uses the samples as its two electrodes and ionizes them by exciting a high frequency, high voltage spark, it becomes necessary to make electrodes suitable for this purpose. The ideal form of electrode is a rod of 1 ~ 3 mm in diameter and 10 ~ 20 mm in length. Its cross-section must not necessarily be a circle. It

must fit the sample holder and be able to excite a spark from its tip.

For the analysis of infinitesimally small sample amounts, one must be careful to avoid undesirable contamination from the outside during the preparation process of samples. The best method of preparation and cleaning is different depending upon the samples, so there is no universal method applicable to all samples. A direct analysis without processing is more desirable for analysis. Appropriate processing is necessary when the surface contamination is to be expected, i.e., when very little knowledge on the previous processing history of the sample is available.

However, reagents used in the processing may cause more contamination, so that great care must be taken concerning the pureness of reagents, their interaction with a residue on the samples and the contamination from processing instruments.

The method of processing is tabulated in the following section.

3.1.1 General Treatment of Samples

(1) It is desirable to use tools having diamond tips to process the samples.

(2) It is better to avoid erosive liquids for rinsing purposes.

(3) When the sample is a monocrystal noble metal, the process of erosion and rinsing is very simple. For example, in the case of silver, it is eroded in nitro-hydrochloric acid and is rinsed with pure water. This process must be repeated more than twice.

(4) When the sample is a very reactive metal, reagents

of high purity must be used, and rinsing must be done very carefully.

(5) When the sample has cracks or when it is porous, it is better to avoid the use of reagents because they may remain within the sample.

(6) When the sample is a very fragile substance, it is better to create a new, uncontaminated surface by cracking it. If the sample is congealed from gas directly, it can be used without further processing.

(7) Typical method applicable to III-V class compounds. This is a good method for arscenic gallium (GaAs).

(a) Remove grease from the sample with solution of xylan and acetone (1:1).

(b) Polish it to the specified size on a glass plate using carborundum (SiC) as a paste made with water.

(c) Wash in pure water after rinsing with acetone.

(d) Erode the sample for one minute in a mixture of hydrochloric acid 3, nitric acid 1, and acetic acid 1, keeping it at the proper temperature.

(e) Rinse with water and remove the acid. /1782

(f) Repeat the processes (d) and (e) and additional two times.

(g) Wash for two minutes in pure water.

(8) It is possible to clean the sample surface by ionic impact.

(9) When the sample is short and its length is not sufficient to use as an electrode, ignite a spark, holding the sample between carbon electrodes. In this case, the direct spark across the carbon electrodes must be carefully avoided. Of course, it is desirable to use carbon electrodes without impurities. Electrodes for spectrum analysis are adequate. When this method is used, the effect of carbon electrodes must be taken into consideration (spectrum lines of carbon or carbide).

(10) Carbon electrodes can be used to support a substance having a low melting point, such as gallium (Ga mp 29.78° C). Drill a small hole in the tip of a carbon bar and insert a small ball of gallium weighing 20 ~ 30 mg. Ignite the spark between two such bars. The gallium will spread itself over the surface, and its spectrum can be obtained. Under favorable conditions, the intensity of the spectrum due to carbon bar may be much weaker than that of gallium and can be neglected. This method is sometimes effective for liquid samples. But it is still a semi-quantitative method because of certain properties of the impurities.

(11) Some metals having a low melting point can be treated by ordinary methods. For example, sodium (Na, mp 97°C) and indium (In, mp 155°C) can be adequately analyzed if overheating of the electrodes is carefully avoided. Metalic tellurium, arscenic and red phosphorus can be directly analyzed, because they are volatile and a comparatively large amount of sample is consumed. However, the ionic source must be cleaned before the next analysis, since there is a

considerable memory effect.

(12) The resistance of samples must be less than $2 \sim 3 \times 10^3 \Omega cm$. Most semi-conductors can be analyzed without any special techniques. In the case of silicon, a direct analysis is possible in our experiment, although the repetition frequency could not be made too high. (A detailed description on semi-conductors is given in 3.1.2.)

(13) In the case of insulators such as silica or glass, carbon bars are attached to them for the purpose of igniting sparks. However, it should be realized that ions are generated from both the sample and carbon bar - as shown in Figure 6.

(14) The application of supersonic waves during the erosion process is very effective. This not only promotes erosion by vibrating the samples, but effects them by cavitation due to the supersonic wave. Therefore, perfect rinsing can be carried out in a very short time during the rinsing process.

(15) When the sample is attached to the device, some researchers have found that the humid state is better for the test (without drying it after rinsing). However, our experience shows that this is not always true.

(16) In order to eliminate contamination on the surface, it is advantageous to run the ionic current for about 15 minutes after the spark is ignited. This not only takes off the dirt on the edge of the surface, but also helps reduce the memory effect of samples by forming a thin film of sample materials over the ionic

source or slit.

(17) The processing of pure aluminum is conducted as follows:

(a) Cut the sample to the specified size with a lathe;

(b) Remove grease in trichlorethylene;

(c) Rinse in acetone, then in water;

(d) Erode in fluoric hydrogen;

(e) Rinse away the acid with water;

(f) Repeat (d) and (e) three additional times;

(g) Rinse for two minutes in running water.

For Aℓ containing impurities, our experience shows that it is better to stop at the process of removing grease and rinsing and not to proceed to the erosion process by acid, because of certain phenomena appearing in the erosion process. The standard sample of aluminum made by Johnson-Matthey Co. was used in our experiment, and this tendency was already observed, even for the impurity content of Aℓ-JM-AB3.

3.1.2 Semi-Conductor Samples (Ref. 13)

The reagents used in processing semi-conductor samples must be of the highest purity and the rinsing water must have the resistance of 8 MΩ. The samples must be handled with tweezers after processing, and they should not be touched by anything but the beaker used for the erosion process.

(1) Indium (In)

(a) Cut to the specified size with a stainless

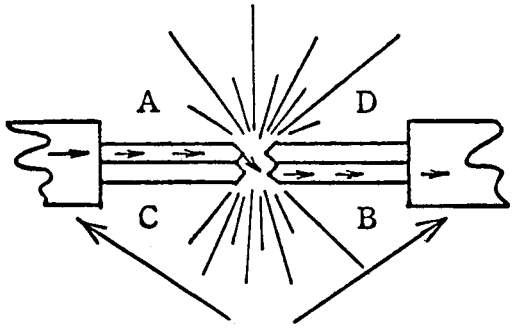

Figure 6

Ignition of the Sparks Between Semi-Conductor Samples

A,B: Conductor (e.g., carbon)
C,D: Semi-Conductor (e.g., silicon)
(1) Sample Holder

knife;

(b) Erode the sample in a pyrex glass beaker filled with 10 mℓ for 30 seconds;

(c) Wash with water to remove grease;

(d) Repeat (b) and (c) three additional times;

(e) Rinse for two minutes by pouring water over it.

(2) Arsenic Indium (In As)

(a) Cut the carborundum paste, which is made by adding pure water to powder, to the approximate size, using a saw of coated tungsten thread;

(b) Remove grease by a 1:1 mixture of xylan and acetone;

(c) Grind the sample to the specified size on a glass plate using a carborundum paste;

(d) Rinse with acetone, then with water;

(e) Put 10 mℓ of water, 5 mℓ of nitric acid and 4 mℓ of oxygenated water into a glass beaker and erode the sample in it (the sample will erode at a rate of 0.01 mm per minute);

(f) Wash with water to remove the acid;

(g) Repeat (e) and (f) two additional times;

(h) Rinse for two minutes in running water

(3) Arsenic Gallium (Ga As)

(a) Follow the operations (a), (b), (c) and /1783 (d) as described for arsenic indium;

(b) Put hydrochloric acid 3, nitric acid 1, and acetic acid 1 into a pyrex glass beaker and erode the sample for one minute in this solution. Warm the solution to the proper temperature;

(c) Wash with water to remove the grease;

(d) Repeat (b) and (c) two additional times;

(e) Rinse for two minutes in running water.

(4) Silicon (Si)

(a) Follow the operations (a), (b), (c) and (d) as described for arsenic indium;

(b) Put the sample in nitric acid in a teflon beaker and introduce drops of fluoric hydrogen until the reaction starts, and for 30 seconds thereafter;

(c) Wash off the acid with water;

(d) Repeat (b) and (c) three additional times;

(e) Rinse for two minutes in pure running water. Rinsing must be carried out right after the erosion process. This also prevents the contamination of the surface by the eroding solution.

(5) Germanium (Ge) (Ref. 14)

(a) Cut the sample to the specified size with a diamond cutter;

(b) Polish on a glass plate using silica (SiO_2) powder;

(c) Wash in pure water;

(d) Put 15 mℓ of nitric acid, 15 mℓ of fluoric hydrogen, and 0.02 mℓ of bromine into a teflon beaker and erode the sample in it for one minute at room temperature. The erosion rate for this solution is 70 μ/min;

(e) Wash in water immediately. When arundum (α-$A\ell_2O_3$) or carborundum (SiC) is used for polishing, their small particles may remain on the sample surface irrespective of the thickness of the surface layer which is removed in the erosive solution. Therefore, silica (SiO_2) powder is recommended for this purpose. Silica powder is also good for semi-conductors which have a surface structure sensitive to polishing.

3.1.3 Powder Sample

(1) When a powder sample of an insulator is analyzed, it is mixed with graphite to make electrodes.

(a) Prepare the same weight of pure graphite powder;

(b) Mix the sample and graphite together uniformly with a mixer;

(c) Make a bar 2 mm square and 20 mm long using a press whose pressure can go up to 10 tons (the pressure differs depending on the kind of sample). Pure silver powder of 99.999% purity is also effective for this application.

(2) Drill a hole at the tip of a pure carbon bar and fill it with powder, then ignite the spark.

(3) Make a sleeve out of plates of pure nickel, gold or platinum and fill it with the sample, then ignite the spark.

3.2 Photographic Dry Plates for the Mass Spectrum

It is necessary to use the dry plates which are highly sensitive to ions in order to be able to detect them. At present, we are using the Q_2 dry plates Ilford. This Ilford Q_2 dry plate was developed jointly by F. W. Aston and the Ilford Co. of England in the 1930's for the purpose of detecting isotopes and is the most suitable one for mass spectral analysis. In addition, information concerning the new Q_2 dry plates has been published recently (Ref. 15), as well as on the SWR dry plate manufactured by the Kodak Co. These have improved blackening properties.

3.2.1 Ilford Q Dry Plate

(1) Property of Dry Plates (Ref. 16)

The emulsion layer of the dry plate is very thin, and its surface is covered by halogenous silver in order to reduce the

absorption of incident ions by gelatine membrane. The use of a chemical for the purpose of increasing sensitivity should be avoided. Thus, it is a special dry plate which extends its sensitive range to the ultraviolet region, and is very sensitive to the ions of heavy atoms. On the other hand, the emulsion surface is very delicate, so that it must be carefully treated, as well as preserved throughout the process of taking photographs.

There are three different types of the Q dry plate:

Q_1: low sensitivity, fine particles, strong contrast, suitable for measuring the ratio of isotopes of elements.

Q_2: medium sensitivity, medium-size particles, suitable for general qualitative and quantitative analysis.

Q_3: high sensitivity, rough particles, weak contrast.

(2) Characteristic Curves (Ref. 16)

According to the characteristic curves of the Q dry plate, Q_2 is best for obtaining a wide range of blackness in linear proportion to the exposive with a satisfactory sensitivity. When the qualitative use of the curve is desired, the relation between the actual exposure ratio and the degree of blackness must be determined for each lot, based on the Churchill curve, which will be explained later.

(3) Minimum Coulomb Sensitivity

According to the Owens report on Q_2 (Ref. 17), visible

blackness is obtained as a line when ions of $1x10^5/mm^2$ reach the dry plate surface under a 15 kV accelerating voltage. If one considers the case when an image having the same width as the main slit (40μ) is focused on the dry plate surface, $0.16x10^6$ ions are necessary to obtain visible blackness as a line, since the length of spectral lines in our device is about 4 mm and the area of a line is equal to $40\mu x4.0mm=0.16mm^2$. Assuming that the ion beam consists of ions of single valence, the total charge of ions is $1.6x10^{-19}$ coulombs. Thus, an /1784 ion beam of $1.6x10^{-19}x0.16x10^5=2.56x10^{-15}$ coulombs is necessary for a sufficient blackness, which requires $0.16x10^5$ ions. If the ratio of the monitoring ion flow for measuring the total exposure and the ion flow which reaches the dry plate is 1:1 (Figure 7), it is possible to detect an element which is contained in the sample having the mol ratio of:

10^{-7} when the total exposure is $1x10^{-8}$ coulomb

10^{-8} when the total exposure is $1x10^{-7}$ coulomb.

However, this is not always true, because such factors as isotopes, the ratio of relative sensitivity, the difference of emulsion surfaces, and the converging property of ions must be taken into account for each case.

3.2.2 Storage Period of Dry Plates

Since the Ilford Q dry plate becomes foggy when it is stored, it can be used for 3 months after the purchase. The following

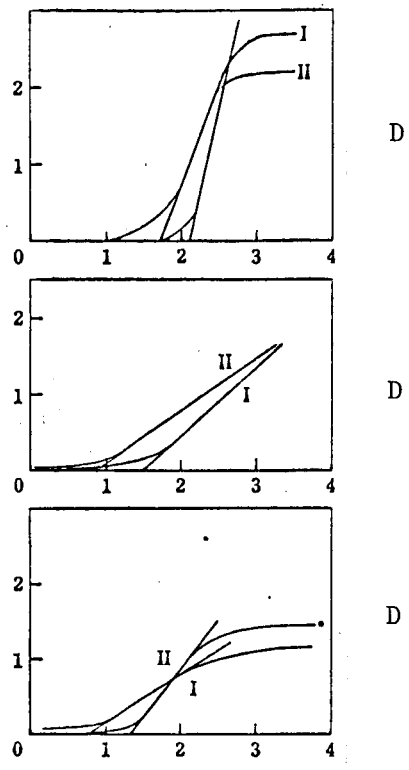

Figure 7

Characteristic Curves of Ilford Q Dry Plates

I: 2.5 min. ID-13
II: 3.5 min. ID-19

instructions must be observed for keeping them in good condition.

3.2.3 Method of Storing Dry Plates

(1) Keep them in a dark, cool place. It is stated that the best temperature is 5 ~10°C. We are using a refrigerator for this purpose.

(2) Treat them very carefully, because their emulsion

layer is very delicate and can be easily destroyed by a careless touch.

(3) Treat the dry plates with care after the photographs are taken, and keep them in good condition.

3.3 Pictures of Spectra

3.3.1 Method of Photographing Spectra

The basic method is the same as in the case of the ordinary dry plate for pictures. Care should be taken to prevent the dry plates from being not only exposed, but also from being scratched on their surface. The basic method for taking pictures is illustrated in the following paragraphs. However, one must consult the individual instruction book, because treatment may be different for each device.

(1) Store the dry plates in the cachet without exposing them or scratching their surface. If possible, they should be placed in a reserve room, after closing the valve of the high-vacuum system inside the analysis tube, and exhaust the room for one night, or at least two hours.

(2) Open the valve, and set the dry plate at the prescribed position in the magnetic field. Then ignite the spark on the sample. Control the spark to be confined within the electrodes and try to prevent overheating. Also, adjust it to increase the ion flow.

(3) When an ion flow is observed and the spark is maintained, interrupt the spark.

(4) Set the indicator of the dry plate at the prescribed position.

(5) Start the spark again. The suitable exposure at this time is less than $1x10^{-13}$ coulomb, in general.

(6) Stop the spark, and set the indicator at the next position; then start the spark once more. The suitable exposure at this time is approximately $\sqrt{10x}$ the previous exposure.

(7) Repeat these operations until the necessary exposure for detection is obtained for one dry plate. If the ratio of exposures becomes too large, the analysis accuracy will be decreased. Thus, the suitable ratio of exposures is about $\sqrt{10}$* for every change.

(8) When the picture is taken, remove the dry plate without exposing it.

(9) Develop the dry plate. The developer suitable for the Q dry plate is ID-19 and ID-13.** Wash with water after the development and use an acid fixative. The time for washing and fixing requires 1/3 to 1/2 of the time for the ordinary dry plate (Ref. 16).

3.4 Mass Spectral Line on the Dry Plate

The components of the sample can be resolved into elements when the spark ionic source is used. Various spectral lines appear as the sum of mass spectra of every element (Ref. 18). Such mass spectrum is simpler than the ordinary spectrum. However, not only the line of the single-valence ion of isotopes, but also the lines of the multiple-

---

* Actually, increase the exposure as follows: 1:3:10.

** According to Instruction for Ilford Q Dry Plates, Rokuoh Shokai Co.

valence ions, ions of multiple atoms and compounded ions can be observed on the spectrum. The details of these spectral lines will be described later.

3.4.1 Spectral Line of Single Valence Ion

When an ion of single valence with a mass M is accelerated, a spectral line appears at the location corresponding to m/e = m, since the dispersion of mass is proportional to m/e in the magnetic field when the number of charges is e. When an element has isotopes (with masses m_1, m_2 and m_3), the single valence ion is recorded at the focuses on the dry plates corresponding to the masses m_1, m_2 and m_3, respectively, with intensities that are proportional to the ratios of the isotope numbers. These lines of single-valence ions have stronger intensities than those of multiple-valence ions or of some other origins.

Example: Silicon has three isotopes of ^{28}Si, ^{29}Si and ^{30}Si. When the number of valence charge is one, their spectral lines appear at the focuses on the dry plate corresponding to m/e 28, 29 and 30, with intensities which are proportional to the ratios of the isotope numbers.

3.4.2 Spectral Line of Multiple-Valence Ion

Since a high voltage having a high frequency is applied to ionize the sample, multiple-valence ions up to 10 valences may be produced from the ionic source besides the single-valence ions. Thus, spectral lines appear at the locations corresponding to m/1, m/2, m/3 ...

on the dry plate. However, the intensity of the line rapidly decreases with the increase of number of charges. It is assumed that the intensity is weakened by 1/5 for every increase of one-valence charge. Therefore, the lines of multiple-valence ions are not observed except for the major component of the sample.

Example: $^{55}M_n$

The spectral lines appear at the locations corresponding to: 55/2 = 27.5 when the valence is 2

55/3 = 18.3 when the valence is 3.

3.4.3 Spectral Lines of Molecules Consisting of Multiple Atoms

The generation of the multiple atom ion formed by 2, 3, or more atoms is rather rare. In general, the smaller the atomic number, the larger the maximum number of atoms that constitute the multiple-atom ion (Ref. 19).

Example: Fe: $^{56}Fe_2^+$ (m=112), $^{56}Fe_3^+$ (m=168), etc.

But the generation of two-atom ions $^{56}Fe_2^+$ is very rare, compared to that of the single-atom ion $^{56}Fe^+$ (Ref. 18). In the case of carbon, silicon and germanium, the lines of their multiple-atom ions are frequently observed. Only the single-valence ions are found on the /1785 spectrum. But the multiple valence ions that appear in the case of single-atom ions are not observed, i.e., the lines of $^{28}Si_2^{3+}$ or $^{12}C_2^{3+}$ are not recognized in the picture.

3.4.4 Spectral Lines of Compound Ions

There are some spectral lines which come from the charged ions consisting of two or more kinds of atoms, although they

are rare.

Example: Spectral lines of $A\ell_2Cr^+$, $A\ell N^+$, FeO^+, $FeOH^+$ and Fe_2O^+.

3.4.5 Spectral Lines Caused by Charge Transfer

When the ions which are generated by the spark discharge are detected in the Mattauch-Herzog type mass spectrometer, very often it is possible to observe the following lines among the spectral lines on the dry plate: the spectral lines of single- or multiple-valence ions of isotopes, the spectral lines of molecules consisting of multiple atoms, the spectral lines of ions having the mass M and the valence charge n+. The latter loses some charges by impact with the residual gas and their charge is reduced to m+, thus yielding spectral lines at the locations $M \cdot n/m^2$ or $M \cdot 1/m$. In this last case, a long tail is frequently spread from the original line towards the side of smaller mass or larger mass. This is a spectral line due to the charge transfer and is frequently observed in the element of the major component.

(1) Charge Transfer Between the Electric Field and the Magnetic Field

Let r be the radius of the ion trajectory having mass M, charge ne and a speed v in the magnetic field H,

$$\frac{1}{2} Mv^2 = neV_a \tag{3-1}$$

$$v = \sqrt{\frac{2neV_a}{M}} \tag{3-2}$$

From the equilibrium of the centripetal force Hnev and the centrifugal force Mv^2/r in the magnetic field, we obtain

$$Hnev = \frac{Mv^2}{r} \tag{3-3}$$

from (3-2) and (3-3)

$$r = \frac{(2V_a \cdot M/ne)^{1/2}}{H} \tag{3-4}$$

Thus, the ions of equal M/ne must be detected at the same point on the dry plate after flying along the same trajectory. If an n-valence ion having mass M_0 impacts a residual gas particle having a mass M_1 and if its charge is reduced to m-valence units without changing its speed, i.e., if the following change takes place,

$$M_0^{n+} + M_1 \longrightarrow M_0^{m+} + M_1^{(n-m)+}$$

then the speed maintained is

$$v = \sqrt{\frac{2neV_a}{M_0}} \tag{3-5}$$

When the same phenomenon takes place between the electric field and the magnetic field, the following relation holds, referring to Equation (3-3)

$$Hmev = \frac{M_0 v^2}{r} \tag{3-6}$$

From this we have

$$r = \frac{(2V_a \cdot M_0 n/m^2 e)^{1/2}}{H} \tag{3-7}$$

Thus, a spectral line is observed at the location as if it were $M/e = (n/m^2 \cdot M_0)/e$. So a sharp line is found at the location n/m^2 corresponding to the mass M_0 before the charge.

(2) Charge Transfer in the Electric Field

Let the charge transfer stated in (1) take place in the electric field. Since a dispersion of the ion beam is caused by the energy of the ion in the electric field of the Mattauch-Herzog type, the intensity of the electric field becomes

$$E = V_E / \ln \frac{r_2}{r_1}$$

where V_E is the applied voltage between two cylindrical electrodes having radii r_1 and r_2, respectively. Since some charges are lost by the charge transfer, the charge of the ion which originally possesses a sufficient energy to pass through the center of the electric field (obtained from the relation between the centripetal force $\frac{V_E}{\ell n \frac{r_2}{r_1}} \cdot ne$ and the centrifugal force Mv^2/r) is reduced from ne to me, so that it cannot pass through the original location at the output slit of the electric field. Since the radius of the ion trajectory in the magnetic field is represented by

$$r = \frac{M/ne \cdot v}{H} \qquad (3\text{-}8)$$

The radius of the ion having small v becomes shorter and it reaches the side corresponding to smaller mass. As the location of the charge transfer changes in the electric field, the trajectory of the ion having a charge me changes also. In any case, it arrives at the side corresponding to the mass smaller than n/m^2 in the case of the charge transfer (1). The closer the location of the charge transfer is to that of (1), the closer the point of arrival is to n/m^2. On the other hand, the

closer the location is to the incident side, the farther the arrival point is from n/m^2, i.e., the side corresponding to smaller mass. Thus the spectrum becomes a continuous spectrum spreading from n/m^2 towards the side corresponding to smaller mass.

(3) Charge Transfer in the Magnetic Field

When this phenomenon takes place at the entrance of the magnetic field, the ion arrives at $n/m^2 \cdot M_0$ as stated in (1). But when it takes place just before impact on the dry plate, a line can be detected at $1/n \cdot M_0$ since there has been no transfer of charge. If the charge transfer is assumed to take place at an arbitrary location within the magnetic field, a continuous background is observed between $1/n \cdot M_0$ and $n/m^2 \cdot M_0$.

Since the starting point of the line is always at $1/n \cdot M_0$ irrespective of n and $n/m^2 > 1/n$ when $m<n$, the background caused by the charge transfer appears at the larger side corresponding to mass larger than $1/n \cdot M_0$ and as a continuous background. But the background due to the charge transfer in the magnetic field becomes weaker than that of the electric field because a restricted amount of the ion beam passes through the entrance slit into the magnetic field. These results are summarized in Table 3.

3.4.6 Aston-band

In 3.4.5, we stated an explanation for the spectral line caused by the charge transfer. A sharp line is observed at the location $n/m^2 M_0$ in the reaction

$$M_0^{n+} + M_1 \longrightarrow M_0^{m+} + M_1^{(n-m)+}$$

TABLE 3

SPECTRAL LINES CAUSED BY THE CHARGE TRANSFER (REF. 18)

Location of Charge Transfer	Spectral Line Due to the Reaction $M_0^{n+}+M_1 \rightarrow M_0^{m+}+M_1^{(n-m)+}$
Between the Electric and Magnetic Fields	a sharp line at n/m^2M_0
Electric Field	a continuous spectrum from n/m^2M_0 towards the side corresponding to smaller mass
Magnetic Field	a continuous spectrum from $1/nM_0$ towards the side corresponding to larger mass

when a charge transfer takes place between the electric and magnetic /1786 fields. However, if there is a stray magnetic field between them, the spectral line may have a certain spread because the effect of the magnetic field on ions changes between the location of the charge transfer and the entrance of the magnetic field. This phenomenon is undesirable because it may reduce the detection limit, appearing as a background. Therefore, the stray field must be eliminated by installing a magnetic shield on this part.

Such spectral lines having a spread due to the charge transfer are called Aston-Bands.

3.4.7 Resolution Necessary for Resolving Multiple Lines

When the mass of an ion is determined, the accuracy is limited to a certain value, depending upon the kind of devices used.

Theoretically

$$\frac{m}{\Delta m_1} = \frac{a_e}{2S_1}$$ when a cylindrical lens is used in an electric field

$$\frac{m}{\Delta m_1} = \frac{a_e}{S_1}$$ when a spherical lens is used in an electric field

where a_e is the radius of the energy selecting device (mm) and S_1 is the width of the main slit (mm).

For example, when a mass spectrometer having the resolution 200 is used, it is sometimes difficult to discriminate $^{208}Pb^+$ from $^{209}Bi^+$. Especially when isobars are present, it is impossible to resolve them without the use of a device having a high resolution because the differences in the masses is extremely small. In the case of $^{54}Cr^+$ and $^{54}Fe^+$, for example, the mass of $^{54}Cr^+$ is 53.9389 (Ref. 21) and $^{54}Fe^+$ is 53.9396 (Ref. 21), and the resolution required for discriminating them is approximately 77,000.

Also, there are some multiple-atom ions or multiple-valence ions whose difference of m/e is very small. For example, the atomic weights of $^{27}A\ell^+$ and $^{59}Fe^{2+}$ are 26.9815 (Ref. 21) and 26.9698 (Ref. 21), respectively, and the resolution required to discriminate them is about 2,300.

Also, in the case of $^{14}N_2^+$ and $^{12}C^{16}O^+$, the weights are 28.0661 (Ref. 21) and 27.9949 (Ref. 21), respectively, and the resolution is 2,600. Thus, the capability of obtaining high resolution spectra becomes the necessary condition for the accurate analysis of spectra.

3.5 Qualitative Analysis of Elements Using the Mass Spectrum

3.5.1 Determination of the Mass-Charge Ratio

In the mass spectrum, many lines which correspond to the mass-charge ratio of atoms examined are shown on a single photographic plate. The mass-charge ratio, m/e, of an unknown atom can be determined by knowing the location of the spectral line. The method (Ref. 20) is as follows. In the Mattauch-Herzog mass spectrometer, the distance ρ from the point at which an ion enters the magnetic field, to a point at which the ion is focused to be a spectral line, is

$$\rho = \sqrt{2}\, r_m = 2 \cdot \frac{(V_a \cdot m/e)^{1/2}}{H} \qquad (3\text{-}9)$$

where r_m radius of ion trajectory, Va: ion acceleration voltage; H: density of magnetic flux; M: mass; e: electronic charge.

(3-9) can be rewritten as

$$\rho = \alpha M^{1/2} \qquad (3\text{-}10)$$

where α is a constant of proportionality, and

$$M = m/e$$

When an unknown sample is analyzed, if some principal elements are already known, they can be detected easily because the spectral lines for their single valence and multi-valence ions appear on the plate in very short exposure time. Let the mass of the principal element be m_s, the number of charge ne and $m_s/ne = M_n$. Two lines are chosen among the spectrum for the element, and m/e corresponding to these lines are marked M_1 and M_2, and ρ corresponding to these M_1 and M_2 are marked

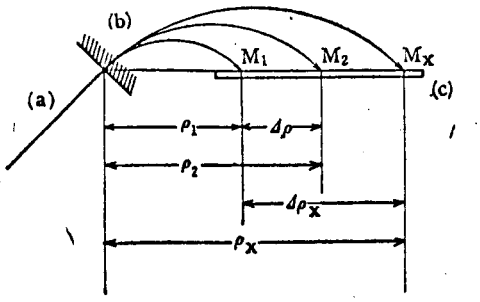

Figure 8

Ion-Beam Trajectories and the Spectral Line in the Magnetic Field

(a)-Ion Beam; (b)-Magnetic Field; (c)-Photographic Plate

ρ_1 and ρ_2, then

$$\rho_1=\alpha M_1^{1/2} \tag{3-11}$$

$$\rho_2=\alpha M_2^{1/2} \tag{3-12}$$

Here, we let $M_2>M_1$ and let the distance between these two lines on the plate be $\Delta\rho$.

$$\rho_2=\rho_1+\Delta\rho \tag{3-13}$$

with (3-11), (3-12) and (3-13)

$$\frac{\rho_1+\Delta\rho}{\rho_1}=\left(\frac{M_2}{M_1}\right)^{1/2}$$

$$\rho_1=\frac{\Delta\rho}{\left(\frac{M_2}{M_1}\right)^{1/2}-1} \tag{3-14}$$

$\Delta\rho$ can be measured on the plate in order to obtain ρ_1. If ρ_χ corresponding to an unknown mass, M_x is expressed by

$$\rho_x=\rho_1+\Delta\rho_x \tag{3-15}$$

and

$$\frac{\rho_1+\Delta\rho_x}{\rho_1}=\left(\frac{M_x}{M_1}\right)^{1/2} \tag{3-16}$$

Therefore

$$M_x=\left(\frac{\rho_1+\Delta\rho_x}{\rho_1}\right)^2 M_1 \tag{3-17}$$

or, by letting $\sqrt{M_x} = k(\rho_1+\Delta\rho_x)$,

$$\sqrt{M_2}=k\rho_2$$
$$\sqrt{M_1}=k\rho_1$$

With these equations,

$$k=\frac{\sqrt{M_2}-\sqrt{M_1}}{\rho_2-\rho_1}=\frac{\sqrt{M_2}-\sqrt{M_1}}{\Delta\rho} \tag{3-18}$$

Therefore

$$\begin{aligned}\sqrt{M_x}&=k(\rho_1+\Delta\rho_x)\\&=\sqrt{M_1}+k\Delta\rho_x\\&=\sqrt{M_1}+\frac{\Delta\rho_x}{\Delta\rho}(\sqrt{M_2}-\sqrt{M_1})\end{aligned} \tag{3-19}$$

Or

$$M_x=(\sqrt{M_1}+k\Delta\rho_x)^2$$

Or

$$M_x=\left[\sqrt{M_1}+\frac{\Delta\rho_x}{\Delta\rho}(\sqrt{M_2}-\sqrt{M_1})\right]^2 \tag{3-20}$$

The value of M_x can be calculated by using one of these three equations. The value of m/e can be determined from the location of the spectral lines on the photographic plate in this way.

When this method is adopted in order to determine /1787 the m/e value for an unknown spectrum, it should be tested in advance whether a linear relation holds between M_n and ρ_n, by measuring the ρ value for a material which was already studied.

3.5.2 Determination of Elements

Using the value of m/e obtained by the method in 3.5.1, the element is determined by the following procedure.

(1) With the m/e value obtained by the method in 3.5.1, isotopes of an element corresponding to each spectral line are guessed by using a mass table (Ref. 21).

(2) The spectral lines for the single and multi-valency ion of the element are observed. One determines whether or not the line intensities correspond to the existence ratios of the isotopes. If this is the case, it can be assumed that the guessed element is the right one.

(3) If the existence ratio of the isotopes and the intensity ratio in the spectrum do not agree with each other, it should be determined whether the lines of the single or multi-valence ions of another element are superimposed on the spectral lines under consideration, especially due to small differences in the m/e values. A multiplet, formed by two or more lines, can be separated if the equipment has enough resolution. Therefore, possible multiplets, which sometimes cannot be separated, must be taken into account. By this reasoning, the equipment should have a high resolution.

(4) Multi-atomic molecular ions, residual gas molecular ions, complex ions and ions produced by charge transfer, which can be expected to appear on the photographic plate, should be taken into account.

3.5.3 Detection Limit

When a sub-element is detected by using the blackness of a spectral line on the photographic plate, the detection limit is not always constant. The limit depends on the kind of the main element and on the characteristics of the equipment. Even if an element is detected as small as 0.01 ppm (in atomic number) by a long exposure, not all the elements contained in the sample can be detected as low as 0.01 ppm. Some spectral lines do not appear on the plate for the following reasons:

(1) A continuous background signal produced by collision between the ions and the residual gas atoms.

(2) A diffusing phenomenon due to the halo effect on the photographic plate which mainly occurs for high-intensity spectral lines.

(3) Spectral lines for the isotopes of the principal elements superimpose on the other spectral lines and mask them by over-exposure. This phenomenon is enhanced when a high-intensity ion beam is photographed in a short time. (This corresponds to the condition where the storage of charged particles on the plate is larger than the number of charged particles leaking along the plate surface.)

(4) The spectral intensity is lowered because the element consists of several isotopes.

(5) The relative sensitivity for the supplement is smaller than that of the principal element (see 3.7).

Since there are several factors restricting detection,

the following calculation method (Ref. 18) is being used to obtain quantitative data. The definitions of a background factor, F_B, and a line factor, F_L, are as follows.

$$F_B = \frac{\text{amount of maximum exposure}}{\text{amount of exposure at which the background just disappears}} \qquad (3\text{-}21)$$

$$F_L = \frac{\text{amount of maximum exposure}}{(\text{amount of exposure at which the spectral lines just disappear}) \times {}^1/_2} \qquad (3\text{-}22)$$

For an element having no isotope, D ppm (atomic) denotes the detectable amount at maximum exposure without the limitation due to background noise. F is the larger of F_B and F_L. Under an assumption that the relative sensitivity and the isotope existence ratio are the same for the principal element and the element under consideration, the detection limit for the element is

$$D \times F \text{ (ppm)} \qquad (3\text{-}23)$$

In general, the other factors should be taken into account, which will be described in 3.6. The detection limit for this case is

$$D \cdot \frac{I_s}{I_t} \cdot \frac{S_s}{S_t} \cdot \frac{A_t}{A_s} \cdot \frac{M_t}{M_s} \cdot F \text{ ppm (atomic)} \qquad (3\text{-}24)$$

For each sample, the detection limit for each element in the sample can be obtained by (3-24). However, this limit depends on the principal element and the equipment even for the same element.

3.6 Qualitative Analysis of Elements With a Mass Spectrum

In order to measure the amount of elements in a sample using the mass spectrum on a photographic plate, a method of observation of the plate (semi-quantitative method) and a method using a microphotometer have been reported. The following method described by Waldron is generally used in practice.

3.6.1 Semi-Quantitative Analysis by Observation (Ref. 18)

This is carried out by the observation of the spectral lines with the naked eye or with a projection screen. One of the isotopes of the element to be analyzed, which just appears on the screen as a mass spectral line, is measured to obtain the content in the sample. This is the quicker and more convenient method.

(1) The use of the spectral line for a single-valency ion: the mass spectral lines for a reference element and an impure (sample) element are produced on the photographic plate. When the line for the single-valency ion is used for the analysis, the content of the impure element is calculated by the following equation.

This equation will also be discussed at the end of this chapter as "a relation between the plate blackening and the amount of the ions generated".

$$\frac{E_s}{E_i} \cdot \frac{X}{100} \cdot \frac{I_s}{I_i} \cdot \frac{S_s}{S_i} \cdot \frac{A_i}{A_s} \cdot 10^6 \text{ ppm (atomic)} \qquad (3\text{-}25)$$

where, E_S, E_i: the amount of exposure at which the spectral line appears on the plate, for the reference element and the impurity element isotope,

respectively. The dimensions are coulombs or a corresponding relative value.

X: the percentage of the isotope of the reference element.

I_s, I_i: the existence ratio of the isotope, for the reference element and the impurity element, respectively.

S_s,S_i: the relative sensitivity* of spectral lines for /1788 single-valency ions, for the reference element and the impurity element, respectively. If the relative sensitivity is unknown, S is set to a constant.

A_s, A_i: the image area of the spectral lines on the plate for the reference element and the impure element, respectively.

(2) The use of spectral lines for a multi-valency ion: when it is difficult to use the image of a single-valency ion for measurement because of background disturbance or other lines, the spectral line for the multi-valency ion, which is not disturbed, can be used For the reference element and the impurity element, the intensity ratio of the spectral lines of the single-valency ion to the multi-valency ion must be known from other experiments in this case. Here M_s is the intensity ratio of the reference element, and M_i is that of the impurity element. Then the percentage of the impurity element is,

$$\frac{E_s}{E_i} \cdot \frac{X}{100} \cdot \frac{I_s}{I_i} \cdot \frac{S_s}{S_i} \cdot \frac{A_i}{A_s} \cdot \frac{M_i}{M_s} \cdot 10^6 \text{ ppm (atomic)} \qquad (3\text{-}26)$$

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* See 3.6.7 and 3.7.

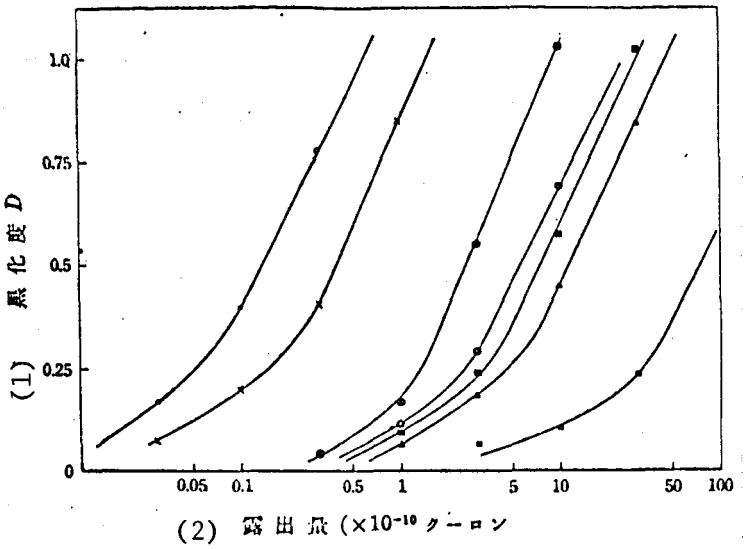

Figure 9

Blackening Curve (from JMS-01)

(1)-Degree of the Blackening D; (2)-Amount of Exposure ($X10^{-10}$ Coulomb)
●: Internal Standard $^{57}Fe^{+}$; x: $^{55}Mn^{+}$; ⊗: $^{32}S^{+}$; ◎: $^{63}Cu^{+}$;
⊠: $^{52}Cr^{+}$; Δ: $^{31}P^{+}$; □: $^{30}Si^{+}$

In addition, when the photographs of each of the spectral lines are taken, the large change in exposure time makes the measurement error larger. Therefore, the change in exposure should be limited to about 3 times (10 db) between each photograph.

3.6.2 A Measuring Method Using a Microphotometer (Ref. 18)

This is a more quantitative method because of no errors in the observation. The degree of the blackening of the isotope spectrum for the reference element and the impurity element are measured by a microphotometer. Figure 9 shows these values vs the logarithm of the exposure. E_s', E_i' are obtained for the same D in the figure, and the content of the impurity in the sample is calculated by the following

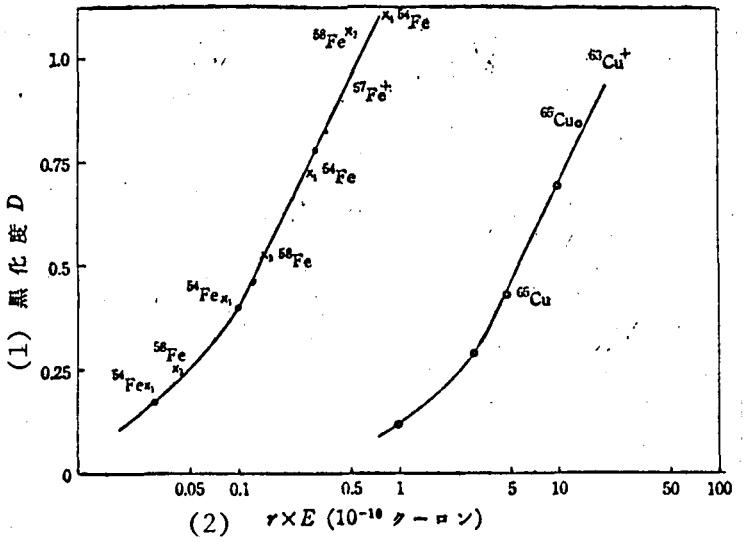

Figure 10

Blackening Curve by the Isotope-Existence Ratio (from JMS-01)

(1)-Degree of the Blackening; (2)-rxE (10^{-10} Coulomb)

equation:

$$\frac{E_a'}{E_1'} \cdot \frac{X}{100} \cdot \frac{I_a}{I_1} \cdot \frac{S_a}{S_1} \cdot \frac{A_1}{A_a} \cdot \frac{M_1}{M_a} \cdot 10^6 \text{ ppm (atomic)} \qquad (3\text{-}27)$$

A linear region in the curves should be used because the curves start to bend at the region of small D due to the characteristic of Q_2 type plates.

3.6.3 Other Methods

In one method, almost the same as the method of 3.6.2, the degree of the blackening is measured by a microphotometer, and a figure is drawn with the logarithm of rxE (the isotope existence ratio and the exposure, respectively) as the abscissa, as shown in Figure 10.

The content is calculated using equation (3-25) and the same procedure is followed in Figure 9.

Kodera and Makita (Kyoto University) and Goto and Kai (Mitsubishi Electric) have published (Ref. 19) much material on analysis using a M. H. type meter.

3.6.4 Atomic Ratio and Weight Percentage

(1) Atomic ratio and weight Percentage

In the equations derived above and marked (atomic) following the equations, the content of the element is obtained as the atomic ratio, namely, the number of atoms of the element under consideration in the sample. The reason is that the number of blackening particles on the plate depends on the number of the incoming ions. However, it is easy to convert the atomic ratio into the weight percentage normally used in chemical analysis. For this purpose, the atomic or molecular weight of the element is used.

The conversion is carried out as follows:

$$W = A \times \frac{I}{S} \qquad (3\text{-}27)$$

where W: Weight Percentage

A: Atomic Ratio

I: Atomic Weight of Impurity Element

S: Atomic Weight of Principal Element

Example: a sample whose principal element is Aℓ is analyzed, and Mn is detected as an impurity (as much as 9.8 ppm (atomic).

Here,

Atomic Weight of Aℓ 26.98

Atomic Weight of Mn 54.94

Therefore,

$$\text{Weight Percentage} = 9.8(\text{ppm}) \times \frac{54.94}{26.98} = 20.4\text{ppm} \fallingdotseq 0.002 \text{ Weight \%}$$

3.6.5 Method Using Churchill's Curve (Two-Line Method) (Ref. 22,23) /1789

When quantitative analysis is carried out with the photographic plates to obtain an accurate relation between the plate blackening and the light intensity, the "Two-Line Method of Emulsion Calibration" due to J. R. Churchill can be adopted.

When this method is applied to spectrum analysis, two spectral lines, whose intensity ratio is 1.2 ~ 2.0, are selected. The degree of blackening of both lines for various exposures are plotted as abscissas and ordinates, respectively. As an example, Figure 11 is taken from a report (Ref. 22) by Churchill.

In the case of the mass spectrography, a pair of mass spectral lines for two isotopes of an element, whose existence ratio is 1.2~2.0, is used and the same type of Churchill's curve can be drawn. By this method, Duke obtained Figure 12 for copper in aluminum by using ^{63}Cu and ^{65}Cu (Ref. 13).

In these curves, if it is assumed that the existence ratio of two isotopes is n, a ratio of the ordinate to the abscissa for

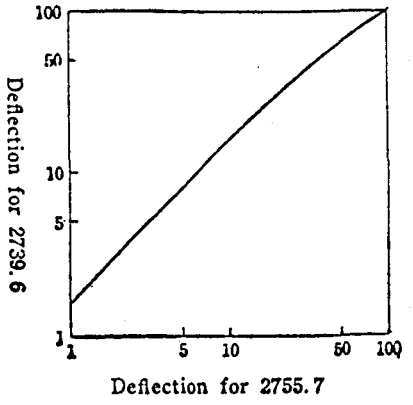

Figure 11

Preliminary Curve Used in Two-Line Calibration Method
Line Pair Fe 2758.7/Fe 2739.6, Intensity Ratio 1.23.

one point on the curve corresponds to the ratio of the blackening under the condition that the exposure ratio is n. At first, take one point A_1 on the ordinate of the curve, and assume the corresponding exposure is 100. The other graph, where the blackening is the ordinate and the exposure is the abscissa, shows an example for $A_1 = 100$. The point A_2 on the abscissa, which corresponds to A_1, is found. As explained above, A_2 is the blackening corresponding to 100n. A_2, 100n is plotted on the second figure. The point A_2 is again plotted on the ordinate of the first curve and A_3, $100n^2$ is obtained in the same way. The result is shown in Figure 13. By doing this once, the ratio of the line intensity is obtained from this curve and the degree of blackening.

3.6.6 Analysis of Microelements Using Seidel's Blackening Method

As in the spectrum analysis, for a region of small

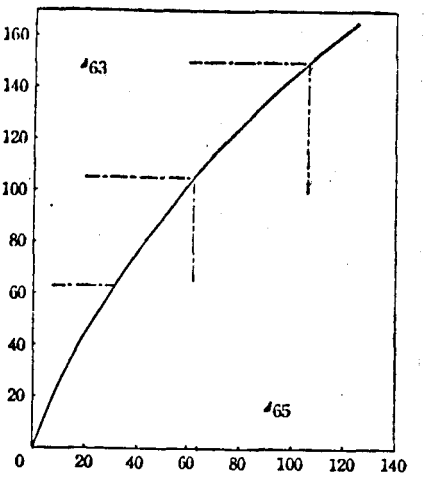

Figure 12
Preliminary Churchill Curve
^{63}Cu 69.1%, ^{65}Cu 30.9%

blackening, the linear region of the blackening curve can be extended further; therefore, very small amounts of the element can be analyzed, using Seidel's blackening method.

In the blackening curve explained above, the exposure is the abscissa and D=log 1/T (D: degree of blackening; T: transparency factor). The ordinate is the blackening. In the region of small blackening, this curve is not perfectly linear, but is S-shaped, because of the characteristic of the photoplate and due to self-absorption of the spectral lines. Therefore, the linear part of the curve must be extended in order to measure very small amounts of impurity. This is done by Seidel's method.

The degree of blackening (Δ) in Seidel's method is

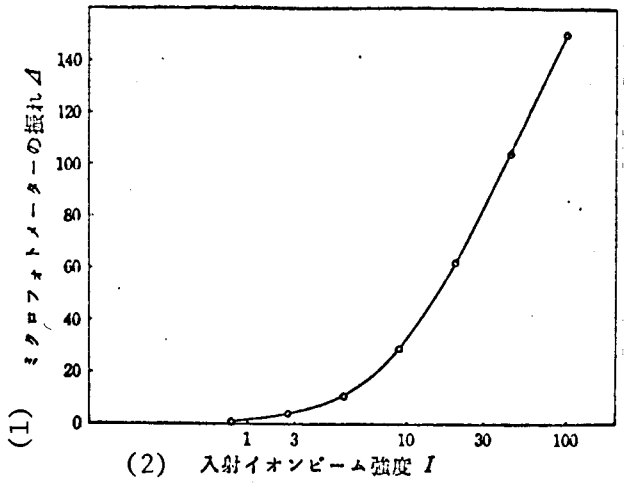

Figure 13

Characteristic Curve of the Q_2 Type Photoplate

(1)-Reading of the Microphotometer, Δ; (2)-Incident Ion Beam Intensity, I.

given as Δ-ℓog (1/T-1). On the other hand, the degree of blackening (D) is usually used as D=ℓog 1/T. Using (Δ), the blackening curve becomes more linear and a more precise measurement of the relationship between the line intensity and the blackening can be carried out. Figures 14 and 15 are examples of blackening curves.

The region that can be analyzed by mass spectrography can be extended to ultra-micro amounts using this method. It is very effective to apply the methods of light spectrum analysis*, which have /1790 a long history, to mass spectroscopy. Important developments in the mass spectroscopy field can be expected.

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* The application of photo spectrum analysis to the mass spectrum field was suggested by Prof. Hitoshi Kamata, Tokyo University.

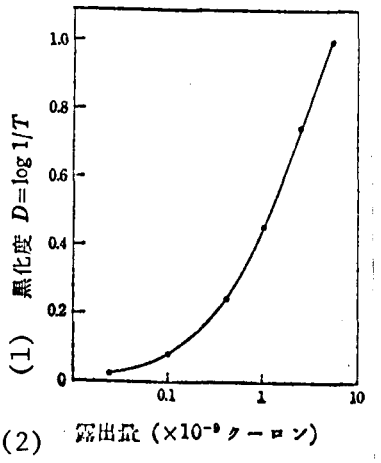

Figure 14

The Blackening Curve

(1)-Degree of Blackening; (2)-Exposure (Multiplied by 10^{-9}).

3.6.7 Blackening of the Plate and Amount of Ions Generated*

A report on this subject, published by H. Hintenberger, is reviewed here. At first, let us consider how the blackening of the photographic plate takes place. Let the number of the ions arriving on a unit area of the plate be D_0, the ion density (the number of ion/cm^2), and assume a linear relation between D_0 and the plate blackening holds. The blackening of the plate is expressed by the density of silver particles d (the number of particles/cm^2) which are reduced by the arriving ions. d depends on the kind, mass number and energy of the ions. These factors are all expressed by k. e is an emulsion factor of the plate. We have:

$$d=keD \tag{3-28}$$

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* The author thanks Mr. Malita for his help in this chapter.

Assume that an element α is contained in a principal element h, and let ${}_hN^+$ be the number of single-valency ions which are generated by h in the ion source, and ${}_aN^{n+}$ the number of n-valency ions generated by α, then we have:

$$ {}_aH_h^{n+} = -\frac{{}_aN^{n+}}{{}_hN^+} \qquad (3\text{-}29) $$

Here, D denotes the ion density of element α which arrive at the plate, K is the ratio of the generated ions to the arrived ions, and b is the width of the spectral line, ℓ is the length of the spectral line, assuming the area of a spectral line is rectangular. Also, ℓ is the length assuming no restriction of the beam falling on the plate surface. The area is then bxℓ; therefore:

$$ {}_aN^{n+} = b \cdot l \cdot D \cdot K_a \qquad (3\text{-}30) $$

From (3-28) and (3-30)

$$ {}_aN^{n+} = \frac{b \cdot l \cdot d}{k \cdot e} \cdot K_a \qquad (3\text{-}31) $$

${}^M_nh$ and ${}^m_ah$ denote the existence ratio of the isotopes of the principal element, h and the impurity element, α, respectively. (3-31) becomes:

$$ {}_aN^{n+} = \frac{{}^m_b n^+ \cdot {}^m_l n^+ \cdot {}^m_a d^{n+}}{k \cdot {}^m e^{n+} \cdot {}^m_a h} \cdot K_a \qquad (3\text{-}32) $$

Here ${}^m_b n^+$ means b-value of the n-valency ion with the mass m, and same notation applies to ${}^m_\ell n^+, {}^m_a d^{n+}$. If only the area b·ℓ is considered in a Mattauch-Herzog type mass spectrometer, the following relation between the mass number m and the b, ℓ values of the n-valency ion holds

$$ {}_{m}b^{n+} = \text{const} \cdot \sqrt{m/n} \tag{3-33} $$

$$ {}_{m}l^{n+} = \text{const} \cdot (A + B\sqrt{m/n}) \tag{3-34} $$

where A and B are constants determined by the equipment. Jansen (Ref. 25) showed that the energy E of an ion whose mass number is m, affects the emulsion factor in the equation,

$$ e = \text{const} \cdot \frac{(E - E_0)}{(m + m_0)} \tag{3-35} $$

Therefore, e is proportional to E when E_0 is small, and is independent of m when m_0 is large.

For the principal element h whose mass number is M, (3-29) can be written as follows.

$$ {}_{a}H^{n+} = \frac{{}_{a}N^{n+}}{{}_{h}N^{+}} = \frac{\sqrt{m/n} \cdot (A + B\sqrt{m/n})(E - E_0)(m + m_0)\,{}^{M}_{m}h \cdot {}^{m}_{a}d^{n+} \cdot K_a}{\sqrt{M}(A + B\sqrt{M})(nE - E_0)(M + m_0)\,{}^{m}_{a}h \cdot {}^{M}_{h}d^{+} \cdot K_h} \tag{3-36} $$

$E_0 \doteqdot 1$ kV, $m_0 \doteqdot 30$ are known (Ref. 25). Here it is assumed that:

1. The ions arrive at a rectangular area,

2. K is unknown, with $K_a/K_h = 1$ because no distinction among ions is made. Using (3-36) the principal element, the impurity, and m, n, h (for the spectral lines), and A, B, E (for the equipment), are obtained. ${}_{a}H^{n+}$ can be calculated knowing d by using a microphotometer. In order to compare the equation with equation (3-25) in 3.6,

the notation of (3-36) is somewhat changed to correspond to (3-25). The right side of (3-36) is expressed by the notation of (3-25), as follows:

$$ {}_{n}H^{n+}=\frac{{}_{a}N^{n+}}{{}_{h}N^{+}}=\frac{m_b^{n+}\cdot m_l^{n+}\cdot m_a d^{n+}\cdot K_a}{k\cdot m_l^{n+}\cdot m_a h}\Big/\frac{M_b^{+}\cdot M_l^{+}\cdot M_h d^{+}\cdot K_h}{k\cdot M_l^{+}\cdot M_h h} \qquad (3\text{-}37) $$

$$ =\frac{m_b^{n+}\, m_l^{n+}}{M_b^{+}\, M_l^{+}}\cdot\frac{M_l^{+}}{m_l^{n+}}\cdot\frac{m_a d^{n+}}{M_h d^{n}}\cdot\frac{M_h h}{m_a h} \qquad (3\text{-}38) $$

where $K_a/K_h=1$.

Here, the principal notation for the principal element h and the impurity α are changed to s (standard) and i (impurity), respectively. We then have

(1) Since $\dfrac{m_b{}^{n+}+m_\ell{}^{n+}}{M_b+M_\ell{}^{+}}$ is the area where the ions arrive, this is expressed again as an area factor A_i/A_s for s and i.

(2) $$\frac{M_\ell{}^{n+}}{m_\ell{}^{n+}} = \frac{(E-E_0)_h/(m+m_0)_h}{(E-E_0)_a/(m+m_0)_a}$$

is the ratio of the blackening depending on the mass and the energy of the ions. But by neglecting mass-dependency and assuming the acceleration leads to the same energy of the ions, this ratio is taken as 1.

(3) Since ${}^{m}_{h}h/{}^{m}_{a}h$ is expressed as a ratio of the isotope existence, I_s/I_i for s and i.

With these factors, (3-36) can be rewritten so as to correspond to (3-26), as follows: /1791

$$ {}_{a}H^{n+}=\frac{A_i}{A_s}\cdot\frac{E_s}{E_i}\cdot\frac{I_s}{I_i}\,, \qquad (3\text{-}39) $$

where ${}_aH^{n+}$ is a ratio of the number of elements to the element i, which are ionized in the ion source of the equipment. The ratio of the amount of the elements in the sample is actually required.

Now assume the number of atoms of the principal element is ${}_hN$, and of the impurity α is ${}_aN$, per unit volume of the sample. The ratio of the generated ions, which have been treated, ${}_aH^{n+}$, is divided by the ratio of the number of atoms ${}_aN/{}_hN$. This value is considered to be relative sensitivity for the element α.

The relative sensitivity, ${}_ag^{n+}$, is then:

$$ {}_ag^{n+} = {}_aH^{n+} \cdot \frac{{}_hN}{{}_aN} = \frac{{}_aN^{n+}}{{}_hN^{+}} \cdot \frac{{}_hN}{{}_aN} \qquad (3\text{-}40) $$

The relative sensitivity depends upon the material. This is due to the fact that the ionization rate depends on the kind of elements, and the influences of the electric and magnetic field around the ionization electrode on the atoms also depend upon the elements. In order to determine ${}_ag^{n+}$, a standard sample whose concentration is known is ionized under constant sparking conditions. ${}^m_ad^{n+}/{}^M_hd^{+}$ are measured for the spectral lines of h^+ and a^{n+}, and are multipled by the area factor, the energy factor and the factor of the isotope existence ratio to obtain ${}_aH^{n+}_h$. On the other hand, the ratio ${}_aN/{}_hN$ for the standard sample is calculated using the known concentration and the molecular weights of two elements. Finally ${}_ag^{n+}$ is obtained by (3-40). If this ${}_ag^{n+}$ is known for every element under consideration, the content of α is obtained by

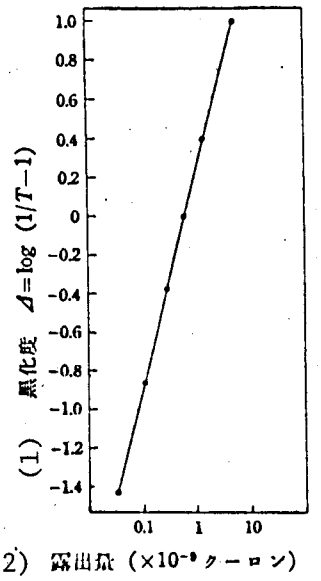

Figure 15

Blackening Curve by Seidel's Method

(1)-Blackening; (2)-Exposure

(Multiplied by 10^{-9}).

$$\frac{{}_aN'}{{}_hN} = \frac{1}{a g^{n+}} \cdot \frac{E_s}{E_i} \cdot \frac{I_s}{I_i} \cdot \frac{A_i}{A_s} \qquad (3\text{-}41)$$

The equation (3-41) is discussed below for the case n=1. (3-41) is written as

$$\frac{{}_aN}{{}_hN} = \frac{1}{a g^{+}} \cdot \frac{E_s}{E_i} \cdot \frac{I_s}{I_i} \cdot \frac{A_i}{A_s} \qquad (3\text{-}42)$$

By dividing by a multi-valency ion factor, the following equation is obtained:

$$\frac{{}_aN}{{}_hN} = \frac{1}{a g^{+}} \cdot \frac{E_s}{E_i} \cdot \frac{I_s}{I_i} \cdot \frac{A_i}{A_s} \cdot \frac{M_i}{M_s} \qquad (3\text{-}43)$$

${}_aN_hN$ also can be obtained from the spectral lines for the multi-valency ions. A proper element is selected as a standard and the

relative sensitivity is obtained for the principal element (S_s), and for the impurity (S_i), both relative to the standard one. The analysis is carried out using (3-26) in the same way as stated above.

3.7 The Relative Sensitivity Ratio and Its Variation

3.7.1 Determination of the Relative Sensitivity Ratio

It has been assumed that all the elements in a sample are ionized at the same rate by a spark discharge in vacuum. Actually, the rate of the ionization depends on the kind of elements (Ref. 18, 26). The biggest rate is about three times as much as the smallest one. This difference of the ionization rate affects the result of the analysis. The relative sensitivity for an element, which is to be measured, is measured in advance, using a proper element as a standard. This is carried out by taking a photograph of the mass spectrum for a sample in which the contents of all the elements are known, and the degree of the blackening is measured by the microphotometer. (3-26), with which the content of elements is calculated, becomes

$$\frac{E_s}{E_t} \cdot \frac{X}{100} \cdot \frac{I_s}{I_t} \cdot \frac{S_s}{S_t} \cdot \frac{A_t}{A_s} \cdot \frac{M_t}{M_s} \cdot 10^6 \text{ ppm (atomic)}$$

in which $M_t/M_s=1$ if the spectral line of the single-valency ion of the isotope is used. The area ratio for two spectral lines is obtainable in advance. Thus,

$$\frac{E_s}{E_t} \cdot \frac{X}{100} \cdot \frac{I_s}{I_t} \cdot \frac{S_s}{A_s} \cdot \frac{A_t}{S_t} = \text{known concentration in ppm (atomic)}$$

gives S_s/S_i, which is the ratio of the relative sensitivity. The relative

sensitivity obtained in this way is, in most cases, 1 ~ 3, and no more (Ref. 18).

A result with aluminum reported by Waldron is shown in Table 4.

TABLE 4

RELATIVE SENSITIVITIES OBTAINED WITH STANDARD ALUMINUM

Elements	Si	Ti	Mn	Fe	Ni	Cu	Zn	
Relative Sensitivity	1.6	1.1	1.8	1.0	0.9	0.8	5.5	(by Waldron)

In the same report, it is stated:

Elements whose relative sensitivity is 1 ~ 3 (Fe=1.0 is assumed):

Bi, W, Ta, Ag, Mo, Zr, Co, Mn, Cr, U, Ti, P, Si, C, B

Elements whose relative sensitivity is more than 3 (Fe=1.0 is assumed):

Pb, Zn, Sn, S, Mg

Another result with using the AEI-MS7 type reported by Sermin is shown in Table 5 (Ref. 26).

TABLE 5

RELATIVE SENSITIVITY (Fe=1.0)

Element	V	Cl	Mn	Co	Ni	Cu	P	S	Sn	As	Pb
Relative Sensitivity	2.86	2.29	2.71	1.32	0.56	0.76	0.54	4.35	1.28	0.67	1.01

(by Sermine)

Thus, there are differences in the sensitivity depending on the elements even if a high frequency spark is used as the ion source. Therefore, the relative sensitivity should be obtained for all equipment in order to obtain better analytical results.

Table 6 shows some relative sensitivities obtained by the author with an aluminum standard sample (Johnson, Matthey) using the JMS-01 type.

TABLE 6

RELATIVE SENSITIVITY (Fe=1.0)

Element	Mn	Zn	Cu	Si
Relative s	2.2	2.9	1.3	3.2
Deviation	+0.1 ~ -0.3	+0.7 ~ -0.5	+0.1 ~ 0	0 ~ -0.1

3.8 Examples of Application of the Mass Spectrum of the Mattauch-Herzog Double Flux Mass Spectrometer

The following sections describe a few examples of micro-analysis. (Iron and germanium.)

3.8.1 An Example of Iron Analysis Measurement

(1) Prior to the photographing of the spectrum, the sample is washed with care so as not to introduce impurities.

(2) A picture of the spectrum is taken, using an Ilford Q_2 type photographic plate. It is exposed 12 times. The conditions are shown in Table 7.

TABLE 7

PHOTOGRAPHING CONDITIONS

No. of Exposure	Amount of Exposure	Pulse Width (μsec)	Repeating Frequency (cycles/s)	Spark Source Voltage (kV)	Acceleration Voltage (kV)
1	$3x10^{-13}$	About 20	1	7	15
2	$1x10^{-12}$	"	"	"	"
3	$3x10^{-12}$	"	"	"	"
4	$1x10^{-11}$	"	10	"	"
5	$3x10^{-11}$	"	"	"	"
6	$1x10^{-10}$	"	100	"	"
7	$3x10^{-10}$	"	1000	"	"
8	$1x10^{-9}$	"	"	"	"
9	$3x10^{-9}$	"	"	"	"
10	$1x10^{-8}$	"	"	"	"
11	$3x10^{-8}$	"	2000	"	"
12	-	-	-	-	-
13	$1x10^{-7}$	"	"	"	"

Development Conditions: /1792

Development: ID-19 solution, temp. 19±0.5° C, for 3 min.

Fixing: Fuji Fix, temp. 18±0.5° C, for 5 min.

Washing: Running (tap) water, temp. 17° C, for 30 min.

(3) Qualitative Analysis: the spectrum obtained and the result analyzed are shown in Figure 16. Detected elements are: B, C, O, Na, Mg, Si, P, S, K, Ca, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As and Se.

(4) Quantitative Analysis:

(a) Drawing the blackening curve: the degree of the blackening is measured for each element by the microphotometer and

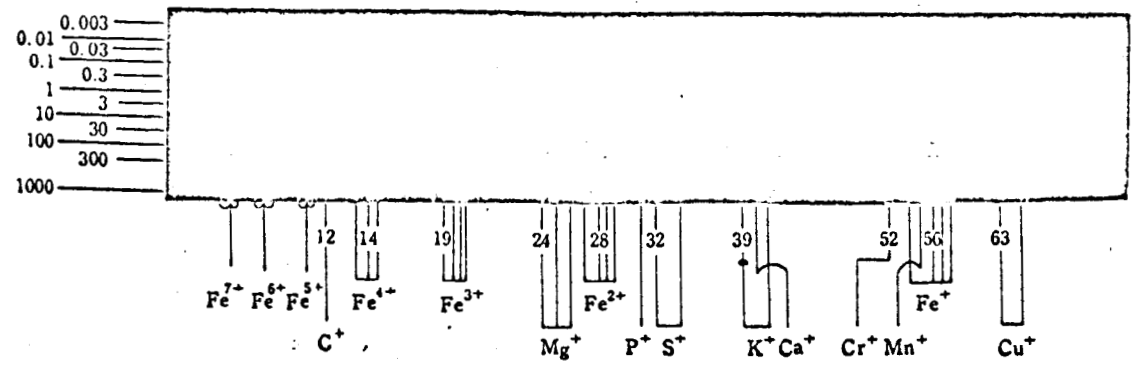

Figure 16

A Part of the Mass Spectrum for an Iron Sample

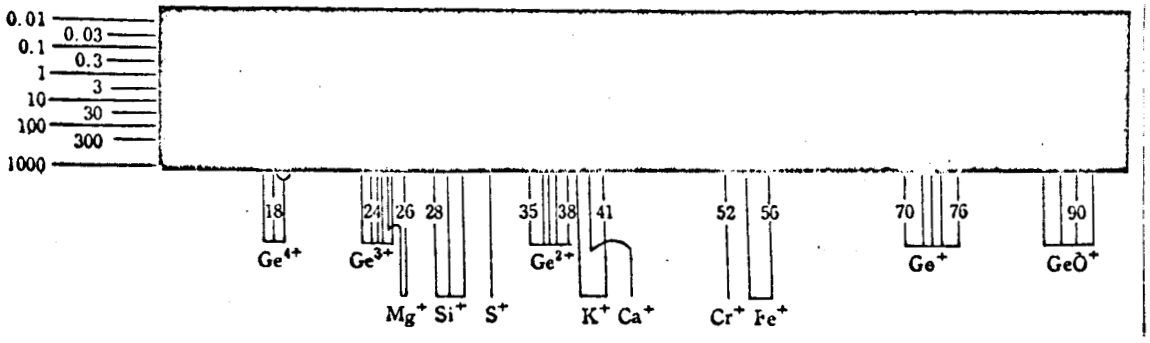

Figure 17

A Part of the Mass Spectrum for a Germanium Sample

the blackening curve is plotted on a graph (see Figure 19).

(b) Concentration of Mn in Fe, shown in Figure 16, is calculated using equation (3-26) as an example.

The concentration of iron is 100% and ^{57}Fe is taken as an internal standard. From Figure 9, when an amount of exposure at which D=0.5 is chosen, then $E_s/E_i = 0.135/0.39 = 0.035$ is obtained. $X = 100$, $I_s = 100$, $I_i = 100$, $M_i/M_s = 1$, A_i/A_s and S_s and S_i are constant, and the Mn concentration becomes 760 ppm (atomic). The weight percentage,

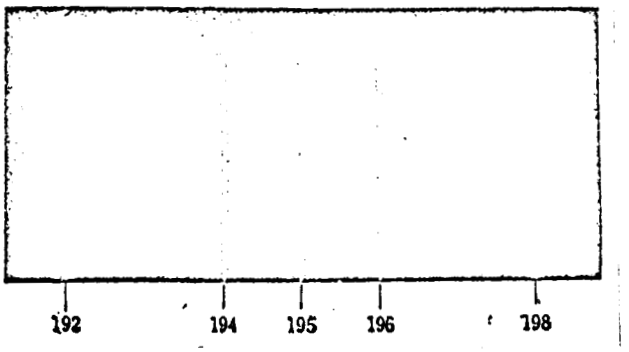

Figure 18

High Resolution Platinum Spectrum

(54.9/55.8)x760, is 750 ppm.

The relative sensitivity of Fe and Mn obtained with the iron standard is 1.0 and 2.5 respectively. Then S_s/S_i = 0.4. By correcting by this value, the concentration of Mn is 300 ppm (weight).

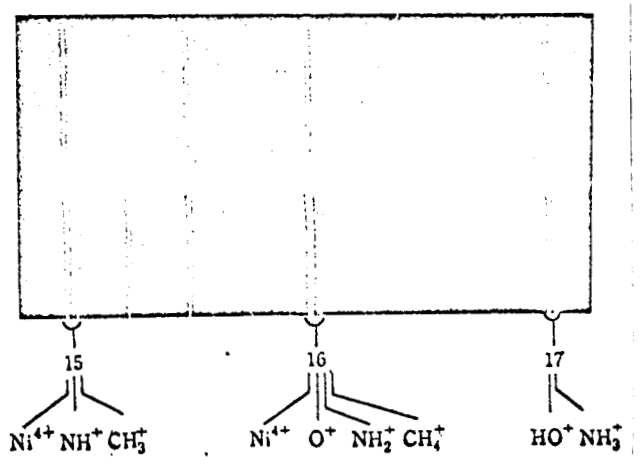

Figure 19

High Resolution Spectrum (Impurities in Au)

The result of Fe analysis is shown in Table 8. /1793

TABLE 8

IMPURITIES IN A Fe SAMPLE

Element	Relative Sensitivity Used (Fe Standard)	Mass Analysis (wt%)	Other Method (wt%)
Si	3.2	0.0041	0.005
P	1.4	0.0068	0.009
S	1.7	0.0006	0.006
Mn	2.5	0.023	0.03
Cu	1.3	0.027	0.004

Considering the minimum amount of exposure stated previously, elements of about $10^{-8\sim9}$ should be detected for an exposure of $10^{-9\sim6}$ coulombs by JMS-01 type meter. Actually, a GaAs sample was analyzed with an exposure of 3×10^{-7}. Several elements in the order of 10^{-9} were detected, especially Li showed a value of 3 ppb.

3.8.2 Other Examples of the Mass Spectrum

Figure 17 is the spectrum of a germanium sample. Figure 18 and 19 are examples of high resolution spectra for impurities in platinum and gold, respectively.

4. Conclusion

Recently, research in various high purity materials is being carried on in industry. The analysis of very small amounts of element are problematical. In this survey the Mattauch-Herzog type mass spectrometer with a spark ion source and its application to analysis were described.

This method is one of the most advanced ones in the field of the micro-analysis. More development in the near future is expected.

The author would like to thank Prof. Shinji Sasaki, Honorable Professor of Kyoto University, and Professor Yuichi Ogata, Osaka University and Mr. Ben Makita, Kyoto University, for their guidance, and also Mr. Yoshio Wada, Division Chief, for his help.

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